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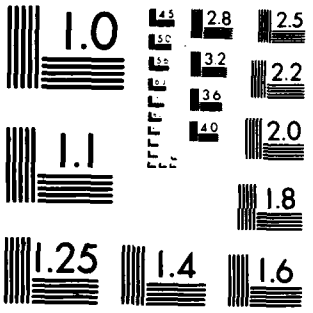

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Laser-Induced Neutralization and Negative-Ion Formation in Surface Scattering

by

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Department of Chemistry
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In neutralization and negative-ion formation from positive ions scattering from a solid surface, a laser can be used to control the nature of resonant, near-resonant, and even non-resonant transfer of electrons from the conduction band. These spectral characteristics can be achieved by variation of only the laser frequency and intensity.

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Laser-induced neutralization and negative-ion formation in surface scattering

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Abstract

In neutralization and negative-ion formation from positive ions scattering from a solid surface, a laser can be used to control the nature of resonant, near-resonant, and even non-resonant transfer of electrons from the conduction band. These spectral characteristics can be achieved by variation of only the laser frequency and intensity.

Introduction

Positive ions impacting on metal surfaces may pick up electrons resonantly or near-resonantly from the conduction band and thus become neutral atoms or negatively-charged ions on recoil.[1-6] These processes usually require that the empty valence level ϵ_d (Figure 1) of the impact-ion be roughly degenerate with the electrons in the conduction band when the ion is in the impact region. If this condition is not fulfilled, neutralization or negative-ion formation can only take place through the much weaker Auger processes.[7] With the introduction of a laser, however, the degeneracy condition ceases to be the determining factor in charge transfer. By varying the laser frequency and intensity, the radiative bound-continuum coupling can readily be manipulated so as to resonantly, near-resonantly, or even non-resonantly transfer electrons from any region in the conduction band to the discrete valence level.

Resonant and near-resonant transfers are effected through the formation of laser-induced metastable states with energies within the band. The degree of resonance is determined by the widths of these states, which, together with the energies, can be controlled by the laser characteristics. Non-resonant transfer is due to the possible formation of a

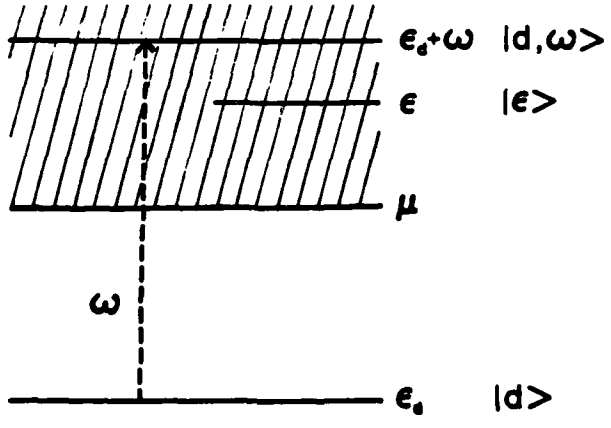

Figure 1. Schematic energy-level diagram for a model ion-surface system interacting with an external laser field near the impact region, where $\hbar\omega$ is the photon energy. The kets denote the states associated with the designated energy levels.

laser-induced bound state with energy below the lower band edge μ. This bound state appears when the laser intensity is raised past a certain frequency-dependent critical value, and the exact location of its energy ϵ_b can also be controlled by the laser characteristics. Of special interest in non-resonant transfer is the onset of the threshold effect when ϵ_b is close to μ, in which electrons are drawn predominantly from near the lower edge of the conduction band.

In the present work, we shall focus on the system's spectral properties responsible for the above effects[8] rather than the dynamics, which has been treated elsewhere.[3-6,9]

Non-resonant transfer

We consider a model for the ion-surface system where field-free energy spectrum near the impact-region is depicted in Figure 1. A radiative bound-continuum coupling $V_{\epsilon\omega}(t)$, peaking around the instant of impact t=0, is responsible for the transfer of electrons from the band states $|\epsilon\rangle$ to the valence state $|d,\omega\rangle$. The quantity that is ultimately of interest is the transfer probability

$$P_{\epsilon d}(t) = |\langle\epsilon|d,\omega;t\rangle|^2, \tag{1}$$

where $|d,\omega;t\rangle$ is the time-evolved state of $|d,\omega\rangle$.

In order to determine $|d,\omega;t\rangle$, it is useful to expand $|d,\omega\rangle$ in terms of approximate eigenstates of the total Hamiltonian. We assume the impact velocity to be low enough such that the adiabatic approximation is valid: the electronic spectrum can be diagonalized independently at each t. The eigenvalue equation is then given by[8]

$$E(t) - \left[\epsilon_d(t)+\omega\right] + g^2 \int_\mu^\infty d\epsilon \frac{\rho(\epsilon)\left|V_{\epsilon\omega}(t)\right|^2}{\epsilon - E(t)} = 0 \ , \ (\hbar=1) \tag{2}$$

where g^2 is a quantity proportional to the field intensity, $\rho(t)$ is the density of states of the band, and it has been assumed that the band is infinitely wide. This equation admits a bound-state solution $\epsilon_b(t) < \mu$, when

$$g^2 > g^2_{crit} = (\omega-\mu+\epsilon_d) \int_\mu^\infty d\epsilon \ \frac{\rho(\epsilon)\left|V_{\epsilon\omega}\right|^2}{\epsilon - \mu} \ . \tag{3}$$

Furthermore, the position of this bound state shifts down as g^2 is increased and/or ω is decreased.

Since this bound state, by definition, cannot be degenerate with the band and can act as a receptor of electrons, it is the origin of a non-resonant transfer term occurring in $P_{\epsilon d}(t)$. An explicit expression [Eq.(8)] for this quantity will be given after we consider the source of the resonant and non-resonant transfer -- the metastable states -- in the next section.

Resonant and near-resonant transfer

When the radiative coupling is weak, a monochromatic laser gives rise to a metastable state centered at $\epsilon_d+\omega+\Delta$ with a width Γ_0, where both the small shift Δ and Γ_0 are proportional to g^2, or the physical field intensity. The presence of this state means that electrons are transferred predominantly from an energy region in the band corresponding to its location and width, hence the designations resonant and near-resonant transfer.

When the coupling is strong, the resonance structure for $P_{\epsilon d}(t)$ becomes much more interesting. In this case the locations of the metastable states have to be determined from the equation[8]

$$E(t) - \left[\epsilon_d(t)+\omega\right] + g^2 \, P[E(t)] = 0 \ , \tag{4}$$

$$P[E(t)] = P\int_\mu^\infty d\epsilon \ \frac{\rho(\epsilon)\left|V_{\epsilon\omega}(t)\right|^2}{\epsilon - E(t)} \tag{5}$$

with P denoting the principal-value integral. The roots of Eq. (4) in general bear no simple relationship to the "unperturbed" line center $\epsilon_d+\omega$, and there may be more than one. Thus, even a monochromatic laser may induce more than one resonance region in the conduction band from which a preponderance of electron transfer takes place. Moreover, one can tune the positions of these regions through the band by varying ω and the field intensity.

There is another interesting complication when the radiative coupling is strong. It is found that[8] the width of a metastable state is not strictly proportional to g^2, but to a "renormalized field intensity"

$$g_R^2 = g^2 / [1 + g^2 P'(E_m)], \tag{6}$$

where

$$P'(E_m) = \frac{d}{dE} P(E)\Big|_{E=E_m} \tag{7}$$

and E_m is the position of a metastable state. For a given physical field intensity and frequency, the conduction band may then be classified according to three regimes. The metastable regime $[P'(E) > 0]$ has the property that the physical width of a metastable state located within it is always smaller than the "bare" width, while for the unstable regime $(-1 < g^2P' < 0)$ the opposite is true. Finally, there may be an unphysical regime $(g^2P' < -1)$ where energies do not correspond to any physically observed states at all, since g_R^2 in this regime is negative.

The electron-transfer spectrum

Neglecting complications due to the collision dynamics, an approximate formula revealing the essential features of this spectrum can be obtained as[8]

$$P_{\epsilon d}(t) = \frac{g^2 |V_{\epsilon\omega}(t)|^2 \beta_b^4(t)}{[\epsilon - \epsilon_b(t)]^2} + \sum_i \frac{g_{Ri}^2 |V_{\epsilon\omega}(t)|^2}{[\epsilon - E_i(t)]^2 + \Gamma_i^2/4}, \tag{8}$$

where the sum is over the metastable states of energies E_i and Γ_i is the physical width given by

$$\Gamma_i = \Gamma_0(E_i) / [1+g^2P'(E_i)] \tag{9}$$

$$\beta_b \equiv \left[1 + g^2 \int_\mu^\infty d\epsilon \, \frac{\rho(\epsilon) |V_{\epsilon\omega}|^2}{(\epsilon - \epsilon_b)^2}\right]^{-\frac{1}{4}} \tag{10}$$

The first term accounts for the main contributions to non-resonant transfer. It is due entirely to the laser-induced bound state and is present only when the physical field intensity is larger than a certain critical value [Eq. (3)]. Since ϵ_b is always less than μ, this term is especially significant near the threshold ($\epsilon \gtrsim \mu$) region and contributes a long-range non-resonant "tail" for large ϵ. The crucial fact is that its importance can always be enhanced by tuning ϵ_b close to μ. We call this the threshold effect due to non-resonant transfer.

The summation term contains contributions to the resonant and near-resonant transfer. Based on the discussion of the previous section, one can also effectively "engineer" the locations and widths of the resonance peaks. Within the metastable regime line narrowing can be enhanced, while in the unstable regime line broadening is facilitated. Moreover, the unphysical regime serves as a filter to block off certain regions of the band from electron transfer.

We stress again that the unusual range of spectral phenomena described by Eq. (8) can all be obtained by a judicious variation of the laser frequency and the physical intensity.

The Anderson correlation energy U

We have shown elsewhere[9] that the Anderson correlation energy U[10] plays an important role in the two-electron transfer process of negative-ion formation. Essentially, U arises from the Coulomb repulsion between two electrons of opposite spin in the discrete valence level, and imposes an energy barrier for the transfer of the second electron once the first electron has been transferred. This condition manifests itself in overall stricter resonance

requirements in resonant and near-resonant transfer than in the neutralization case. Hence, in light of the uncertainty principle, short interaction times, or equivalently, large impact velocities are in general favored.

The laser can again be tuned to advantage in this situation. Without arbitrarily increasing the impact velocity of the positive ion, one can either make use of the bound state to enhance the non-resonant part of the transfer, or make use of a "metastable" state in the unstable regime to relax the resonance requirements, or use a suitable combination of the two effects. If, in addition, one can "probe" the spectrum on very short-time scales (on the order of typical collision times) so that resonance requirements are lax even in the field-free case, the barrier effects of U may be largely overcome. This probing can again be best achieved by a laser -- one with pulse durations on the order of collision times.

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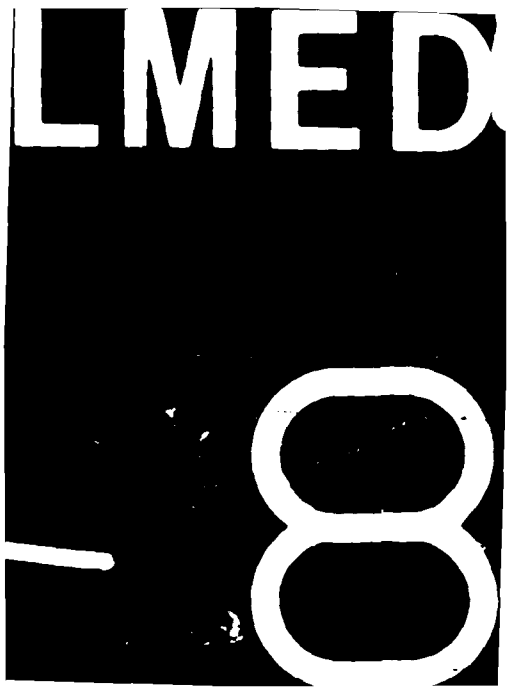
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